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REFINING OF THORIUM - CONTAINING URANIUM CONCENTRATES BY EXTRACTION WITH TRIBUTYL PHOSPHATE

Written by

Carl W. Huntington

Work Performed by

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of

TECHNICAL DIVISION
NATIONAL LEAD COMPANY OF OHIO

August 29, 1957

Approved By:

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1.0 ABSTRACT

A method of refining thorium-containing uranium concentrates by extraction with tributyl phosphate has been developed from laboratory and pilot plant data and has been demonstrated in the National Lead Company of Ohio Refinery. In the separation of thorium and uranium by tributyl phosphate, complications arising from the high selectivity of the solvent for both elements have been overcome by the use of phosphate for preferentially complexing the thorium in the aqueous feed slurry. Specification product (<50 ppm thorium, uranium basis) can be obtained from feed materials containing as much as 2 per cent thorium (U_3O_8 basis), if the feed slurry contains 15 per cent phosphate (uranium basis). Other approaches to thorium-uranium separation were found to be less successful than phosphate complexing and are reported briefly.

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2.0 INTRODUCTION

Of the large number of metal nitrates which exhibit solubility in tributyl phosphate (TBP), uranyl nitrate and thorium nitrate are the most soluble; of these two, the latter is only slightly less soluble than the former.[1] Liquid-liquid extraction with tributyl phosphate has consequently become a prime method for the purification of uranium and thorium salts.[2,3] Because of the high selectivity of the solvent for both metals, special separation techniques must be utilized when one is present as an impurity in the extraction feed stream of the other. Until the last two years, this problem was not prevalent in the production of uranium but was encountered chiefly in the development of processes for the purification of thorium.[4,5]

In the latter part of 1955, it became apparent that future receipts of uranium concentrates in the United States would be comprised of increasingly large amounts of material from Canadian sources in which the uranium is found in association with large amounts of thorium. Although ore concentration processes – such as the Bicroft operation in the Bancroft mining area of eastern Ontario, and the Pronto, Algom-Quirke, and Algom-Nordic plants in the Blind River area – effect a gross decontamination of thorium from uranium, the concentrates derived from these ores contain appreciable amounts of thorium.

The Feed Materials Division of the USAEC imposed a maximum limit of 50 ppm thorium (on a uranium basis) for orange oxide (UO_3) produced through the provisions of the Civilian Applications Program.[6] The USAEC Joint Committee on Uranium Concentrate Specifications developed and recommended a maximum level of 2 per cent thorium on a U_3O_8 basis for uranium concentrates.[7] A thorium decontamination factor of at least 470 must therefore be achieved to obtain specification product from feed materials containing the 2 per cent thorium concentration.

The Refinery process at the National Lead Company of Ohio involves the countercurrent extraction, in pulsed, plated columns, of uranyl nitrate by a solvent stream composed of 33.5 volume per cent tributyl phosphate in kerosene. The processing of thorium-bearing uranium concentrates in this system was thus expected to present considerably more purification problems than are encountered with other high-grade concentrates. Until this time, the thorium content of uranium feeds supplied to this refinery was insignificant and hence did not present an operational problem. A program was therefore initiated to develop an economical method of processing thorium-containing uranium concentrates at this site.

The existing data from other sites relative to the partitioning of thorium and uranium by TBP extraction are not directly applicable to the National Lead Company of Ohio extraction system. A separation is achieved in the Thorex process;[5] however, this process was developed to separate small amounts of uranium from large amounts of thorium, the converse situation from that which exists in uranium refining. Work at another site with a refinery system similar to the National Lead Company of Ohio system indicated that separation of thorium from uranium by solvent extraction with 22½ per cent TBP is possible if a high degree of uranium concentration (approaching saturation) is maintained in the organic extract. The extraction columns at that installation are longer than those at this site, however, and the uranium extract conconcentration levels used cannot be attained in the National Lead Company of Ohio system without excessive raffinate losses.

Approaches considered in the development of this program included head-end treatment and extraction process changes. Extraction equipment modifications constituted another possibility but were not necessary.

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This report describes the various phases of the development effort at the National Lead Company of Ohio, which culminated in the successful plant application of a phosphate-complexing method by which specification orange oxide (<50 ppm Th, U basis) can be produced from uranium feed slurries containing 2 per cent thorium (U_3O_8 basis) by a one-cycle extraction process with tributyl phosphate.

[redacted]

3.0 EXPERIMENTAL DETAILS AND DISCUSSION OF RESULTS

3.1 CONCENTRATES USED IN THIS STUDY – Pronto concentrate is produced by the neutralization and precipitation of ion-exchange eluate by MgO. Various quantities of four lots of Pronto concentrate (P-1, P-6, P-16, and P-26) were received for laboratory and pilot plant development tests. Typical analyses for the four lots are presented in Table I.

TABLE I

COMPARATIVE ANALYSES FOR LOTS OF PRONTO CONCENTRATE

Constituent	Lot Number			
	P-1*	P-6**	P-16**	P-26**
U (%)	55.26	53.16	45	41
Th (%)	0.94	0.85	0.78	0.93
Th (%, U basis)	1.71	1.60	1.73	2.27
Ca (%)			1.48	3.55
Mg (%)	3.46		6.46	12.79
PO_4 (%)	2.4		1.92	1.5
Cl (%)	0.2	0.048		
F (%)	0.01	0.06		
Ag (ppm)	<10			
Al (ppm)	1,000-10,000	400	350	4,000
As (ppm)	–	<100	<100	
B (ppm)	10-100	40	4	100
Ba (ppm)	–			<200
Bi (ppm)	<10	<20	20	
Ca (ppm)	1,000-10,000			10,000
Cd (ppm)	–			
Co (ppm)	100-1,000	<10	<10	<400
Cr (ppm)		<10	<10	<200
Cu (ppm)	10-100	<100	<100	<600
Fe (ppm)	10,000-100,000	40,000	40,000	>60,000
Mg (ppm)	10,000-100,000	>>8,000	>>8,000	40,000
Mn (ppm)	100-1,000	400	300	2,000
Mo (ppm)	10-100			<400
Na (ppm)	1,000-10,000			
Ni (ppm)	<10	30	50	<200
P (ppm)	–	7,000	4,500	
Pb (ppm)	100-1,000	150	150	
Sb (ppm)	–			
Si (ppm)	10,000-100,000	3,200†	3,700†	>120,000†
Sn (ppm)	–	<10	<10	<200
Sr (ppm)	10-100			
Ta (ppm)	–			
Ti (ppm)	1,000-10,000			6,000
V (ppm)	10-100	<100	<100	<400
W (ppm)	–			
Y (ppm)	–			
Zn (ppm)	–	<200	<200	<400
Zr (ppm)				

* Analyses performed by New Brunswick Laboratory
** Analyses performed by National Lead Company of Ohio
– not detected
† SiO_2

[redacted]

Successive lots of Pronto concentrate presented increasing difficulties in extraction, because of emulsification. Lot P-1 was used only in laboratory work (Sections 3.2.3 and 3.2.4) and could be extracted without physical difficulty if the digest slurry were filtered. Lot P-6 was used in preliminary pilot plant tests (Section 3.2.5), and the feed slurries from this lot were extracted without significant difficulties. The first extraction test with Lot P-16, however, had to be terminated because of emulsification of the entire extraction column; it was later determined that the emulsification could be prevented by altering the start-up technique (Section 3.5.2.2). Lot P-26 could not be extracted in the pilot plant columns under any conditions because of emulsification with the solvent (Section 3.5.2.2). At the time these tests were in progress, the Mallinckrodt Uranium Division reported in informal communications that similar difficulties had been encountered with Pronto feed slurries. Because of this factor and the fact that other thorium-containing concentrates were not available, the final pilot plant demonstration test in this investigation (Run 328) was made with a $Th(NO_3)_4$-spiked feed stream.

Shipments of Pronto and other concentrates received later for Refinery processing proved amenable to pulse column extraction, however. The plant demonstration data presented in Section 3.6 is based upon a feed slurry composed of Pronto concentrate, Colorado concentrates, and black oxide. To date, the phosphate-complexing method has been successfully used with a variety of other thorium-containing concentrates, such as Algom, Bicroft, Faraday, Denison, and Porter Brothers. Characteristic analyses of these concentrates are given in Table II.

3.2 PRELIMINARY INVESTIGATIONS – To prepare for the processing of thorium-bearing uranium concentrates at the National Lead Company of Ohio, it was necessary first to determine the thorium tolerance of the National Lead Company of Ohio Refinery. Small quantities of Pronto concentrate, Lots P-1 and P-6, were received for preliminary laboratory and pilot plant testing. This material was a very finely divided powder which contained approximately 54 per cent uranium and 0.9 per cent thorium, with iron, silica, phosphate, magnesium, and sodium as the chief impurities (Table I).

3.2.1 Summary of Results – Existing procedures were found to be adequate for the determination of uranium, thorium, and nitric acid in solutions containing all three components (Section 3.2.2). The Pronto concentrate received for preliminary work was digested with nitric acid without difficulty (Section 3.2.3). Extraction of Pronto feed slurries in laboratory funnels was complicated by emulsification difficulties (Section 3.2.4); however, this

TABLE II

TYPICAL ANALYSES OF SOME THORIUM-CONTAINING URANIUM CONCENTRATES

Constituent	ALGOM Chem Ppt.	BICROFT Chem Ppt.	DENISON Chem Ppt.	FARADAY Chem Ppt.	PORTER BROS. Chem Ppt.
Uranium (%)	66	54	59	56	65
Thorium (%)	0.36	0.46	0.07	0.60	2.0
PO_4 (%)	0.74	0.31	0.17	0.83	0.1
SO_4 (%)	3.81	0.42	0.97	0.40	0.04
Cl (%)	0.01	0.01	0.22	0.04	0.04

[redacted]

trouble was not encountered in pilot plant column extraction tests (Section 3.2.5).

Preliminary laboratory and pilot plant work established the following items:

1. Extraction of concentrates containing the expected maximum thorium content (2 percent Th, U_3O_8 basis) under the standard 33.5 percent TBP flowsheet conditions results in a decontamination factor of six (Section 3.2.5.1).

2. Thorium-containing uranium concentrates such as Pronto must be blended approximately 1 to 12 on a uranium basis with other high-grade concentrates to meet the product specification for thorium (Section 3.2.5.2).

3. Thorium decontamination can be increased by increasing the uranium content of the organic extract stream; however, losses of uranium in the aqueous raffinate stream also increase. Raffinate losses might be minimized by refined control of the organic density profile in the extraction column (Section 3.2.5.3).

3.2.2 Analytical Procedures – Before laboratory extraction tests were begun, it was necessary to check a number of analytical procedures to determine their applicability to solutions containing both uranium and thorium.

The determination of thorium in uranium-bearing solutions was made by a colorimetric method, with thoron as the indicator.[8] Pretreatment of the sample involved the separation of the thorium in solution by precipitation as the fluoride, using lanthanum as a carrier.[9] This is followed by perchloric acid fuming to remove interfering anions and then by the colorimetric determination of thorium. The method was found to be satisfactory if the diluted samples were analyzed immediately; if the samples were allowed to stand, an apparent loss of thorium was experienced. Therefore, the original sample (rather than a diluted aliquot) was always rechecked. Although reliable results can be obtained by proper application of this procedure, the method is rather lengthy and, to a certain extent, tedious. Thorium analyses for all laboratory and pilot plant tests were made by this method.

The effect of thorium on the thiocyanate colorimetric determination of uranium was investigated, and no appreciable interference was found at uranium/thorium ratios of 200/1 to 1/6. It was therefore concluded that this method could be used in the investigation.

Since the presence of thorium has a quenching effect upon the fluorometric determination of uranium, samples with low concentrations of uranium were passed through an ion-exchange column containing Dowex A-1 resin to effect a thorium-uranium separation. The uranium was preferentially adsorbed on the resin and was subsequently eluted and analyzed. Work upon control samples indicated that a uranium loss of approximately 1.5 per cent occurs in the ion-exchange separation process.

It was also established that the $K_2C_2O_4$ method for the determination of free acid in uranyl nitrate streams may be used without interference from the thorium.

3.2.3 Laboratory Digestion Tests – Laboratory digestion tests showed that Pronto concentrate could be digested without difficulty. Typical digestion data obtained by the use of Lot P-1 are presented in Table III (Experiments 1 to 3).

The digestion reactivity with nitric acid was mild, which permitted a rapid rate of concentrate addition. The small volume change observed (initial volume/final volume = 0.979) was indicative of a mild reaction. The acid consumption factor (0.011

[redacted]

TABLE III

DIGESTION OF LOT P-1 PRONTO CONCENTRATE

	Experiment No.			
	1	2	3	4
Wt of Feed (g)	104	174.8	357.8	358
Volume of dilute HNO_3 (ml)	500	500	979	980
Conc. of dilute HNO_3 (N)	8.0	7.2	7.1	7.1
Vol of 15.8N HNO_3 required (ml)	253	228	434	439
Time required for ore addn. (min)	8	5	15	30
Total digestion time (hr)	2	2	2	2
Initial temperature (°C)	43	42	46	—
Final temperature (°C)	52	62	62	—
Volume of final slurry (ml)	500	515	1000	988
Slurry Analysis				
g/l uranium	119	187	201	202
N HNO_3	5.6	3.4	3.2	3.3
Acid Consumption Factor (equiv. HNO_3/g ore)	0.012	0.011	0.011	
Volume Change Factor (V_I/V_F)*	1.000	0.979	0.979	0.999
Dry wt of slurry solids (g)				13.8
Solids content of slurry (g/l)				14
Acid-insoluble content of concentrate (%)				3.86
Analysis of Slurry Solids				
U (%)				0.26
Th (%)				0.14
Unconverted Uranium (%)				0.018

* V_I/V_F = Initial volume/Final volume

equivalents of HNO_3 per gram of concentrate) was comparable to that for other high-grade concentrates. The slurry gave no evidence of post-digestion reactivity after the two-hour digestion period. One sample of slurry was allowed to stand overnight, and a light gel formed. A large part of the solids remaining in the slurries were so light that they remained suspended.

Another digestion test was made to obtain quantitative data on the slurry solids (Experiment 4, Table III). The test showed that the acid-insoluble content of the slurry was 14 g/l, or 3.86 per cent of the weight of concentrate digested. The actual solids content of the slurry was much lower than visual observation would predict, because of the light, flocculent nature of the particles. The solids contained 0.26 per cent uranium and 0.14 per cent thorium. The unconverted (undigested) uranium value, 0.018 per cent of the total uranium, was well within the National Lead Company of Ohio specification of 0.05 per cent.

3.2.4 Laboratory Batch Countercurrent Tests — Three batch countercurrent extraction tests were made with aqueous feed derived from the digestion of Pronto concentrate. The flow ratios approximated those of the 33.5 per cent TBP flowsheet (feed/organic/scrub = 5/9/1). The first test, made with a slurry feed, was terminated after one volume change because of severe emulsion difficulties. A portion of the slurry was then filtered and carried through six extraction stages; no emulsification

[redacted]

troubles were encountered with the clarified solution. The remaining tests were therefore made with filtered feed.

The second batch countercurrent extraction test (Table IV) was made without difficulty through three volume changes (36 equilibrations), which is the standard laboratory extraction test. Material balance calculations for both extraction and scrub sections show a 99.5 per cent closure (out/in) for uranium values, but only a 12 per cent closure for thorium. Thus, while the uranium distribution in the system approached equilibrium in 36 equilibrations, the thorium distribution was quite far removed from steady-state conditions.

After 36 equilibrations had been made in a third batch countercurrent extraction test, each phase was sampled for analysis. The test proceeded with the remaining portions at the proper flow ratios through 56 equilibrations (5 volume changes). The results (Table V) again show that the uranium had approached equilibrium (104 per cent and 107 per cent closures at 36 and 56 equilibrations, respectively), but that a buildup of thorium in the system was still progressing after five volume changes (8 per cent and 14 per cent closures at 36 and 56 equilibrations, respectively).

Examination of the stage data for the "compound column" represented by the batch countercurrent scrub and extraction sections (Table IV and V) shows a thorium "bulge" in the center of the column, with indications that the thorium concentrations would increase in both directions as equilibrium were approached. Since the final organic extract contained approximately 50 ppm thorium (U basis), it was evident that the thorium

TABLE IV

BATCH COUNTERCURRENT EXTRACTION OF LOT P-1 PRONTO CONCENTRATE

Volume Ratios F/O/S* = 5/9/1

Volumes Feed = 150 ml; Organic = 270 ml; Scrub = 30 ml

Equilibrations 36

Feed 191 g/l U; 3.21N HNO_3; 3.35 g/l Th

Solvent 33.5% TBP in Kerosene (Shell Dispersol)

Scrub Distilled H_2O.

Stage No.	Sp. Gr. (25°/25°C)		Acid Normality			Uranium Conc. (g/l)			Thorium Conc. (g/l)		
	Aqueous	Organic	Aqueous	$E\frac{O}{A}$	Organic	Aqueous	$E\frac{O}{A}$	Organic	Aqueous	$E\frac{O}{A}$	Organic
4S	–	0.9874	–		0.05	134.7	7.038	105.3	0.037	0.252	0.001
3S	–	1.0044	0.22	2.862	0.07	140.7	7.506	117.3	0.43	0.126	0.006
2S	–	1.0193	0.70	1.026	0.08	149.3	7.110	118	1.98	0.162	0.036
1S	–	1.0103	1.78	0.603	0.12	79.3	5.913	120.7	7.59	0.216	0.179
1E	1.2952	1.0035	3.90	0.084	0.22	25.6	6.680	114	22.0	0.052	0.78
2E	1.2472	0.9142	4.19	0.276	0.77	2.20	13.09	19.2	11.9	1.538	12.2
3E	1.2362	0.8838	4.29	0.350	1.0	0.016	51.57	0.550	4.36	2.376	6.91
4E	1.2243	0.8747	4.0	0.386	1.03	0.007	13.65	0.055	1.66	2.050	2.27
5E	1.2267	0.8730	4.10	0.374	1.02	0.007	6.75	0.031	0.62	2.104	0.87
6E	1.1941	0.8701	2.89	0.456	0.88	0.005	7.8	0.027	0.23	1.695	0.26

* F/O/S = Feed/Organic/Scrub

[redacted]

specification for the product would be greatly exceeded at equilibrium.

The failure of thorium to attain equilibrium distribution in the above tests is consistent with the behavior of thorium in other TBP systems. Difficulties were encountered during the Thorex process development program in determining steady-state concentrations of thorium.[10] Batch countercurrent tests of long duration are impractical because of the time and manpower required to complete them; in addition, a high incidence of failures may be expected due to operating error during the numerous and tedious separations.

In view of these difficulties, it was decided to conduct further extraction work in pilot plant equipment.

3.2.5 Pilot Plant Six-Inch Column Extraction Tests – A full description of the pilot plant six-inch column system has been published;[11] it includes 3 six-inch-ID columns, each having an effective height of 25 feet. The extraction and scrub columns, which are primarily of stainless steel, are plated pulse columns similar to the Refinery columns. The re-extraction column, however, is a glass jet-mixer column whose performance cannot be directly compared with that of the Refinery strip column.

The six-inch system also includes digestion facilities, a solvent treatment process, and boil-down equipment. With the exception of the strip column, it is nearly a prototype of the Refinery system. Its chief disadvantage is that a large amount of feed is required for each extraction test.

3.2.5.1 Decontamination of Thorium Effected by the 33.5 Per Cent TBP Flowsheet (Run 316) – The first test in this series was designed to determine

TABLE V

BATCH COUNTERCURRENT EXTRACTION OF LOT P-1 PRONTO CONCENTRATE

Volume Ratios F/O/S = 5/9/1

Volumes Feed = 75 ml; Organic = 135 ml; Scrub = 15 ml

Equilibrations 56

Feed 191 g/l U; 3.26N HNO_3; 3.35 g/l Th

Solvent 33.5% TBP in kerosene (Shell Dispersol)

Scrub Distilled H_2O

Stage No.	Sp. Gr. (25°/25°C)		Acid Normality			Uranium Conc. (g/l)			Thorium Conc. (g/l)		
	Aqueous	Organic	Aqueous	$E\frac{O}{A}$	Organic	Aqueous	$E\frac{O}{A}$	Organic	Aqueous	$E\frac{O}{A}$	Organic
4S	–	0.9889	0.08	2.392	0.023	139.3	6.975	108.0	0.080	0.612	0.0054
3S	–	1.0062	0.21	1.845	0.043	161.3	6.363	114.0	0.52	0.171	0.010
2S	–	1.0103	0.63	0.828	0.058	144.0	7.578	121.3	3.53	0.126	0.050
1S	–	1.0094	1.73	0.086	0.098	81.3	13.428	121.3	12.42	0.180	0.255
1E	1.3132	1.0055	3.80	0.090	0.23	23.5	7.02	110.0	36.7	0.050	1.21
2E	1.2604	0.9196	4.23	0.252	0.71	2.05	12.29	16.8	17.25	3.422	39.35
3E	1.2398	0.8778	4.25	0.363	1.03	0.008	117.15	0.625	6.25	2.544	10.6
4E	1.2412	0.8892	4.29	0.328	0.94	0.004	1.125	0.030	2.35	2.541	3.98
5E	1.2405	0.8742	4.95	0.306	1.01	0.003	6.45	0.013	0.85	1.659	0.94
6E	1.1993	0.8673	2.82	0.468	0.88	0.004	2.25	0.006	0.33	2.205	0.485

[redacted]

the decontamination of thorium which is achieved by standard operation of the 33.5 per cent TBP extraction flowsheet with feed containing approximately 2 per cent thorium (U_3O_8 basis).

Since sufficient Pronto concentrate to make this test was not immediately available, thorium nitrate was added to uranyl nitrate feed derived from the routine nitric acid dissolution of massive scrap uranium metal. The stream concentration and the nominal test conditions are shown in Table VI.

TABLE VI

RUN CONDITIONS FOR PRELIMINARY PILOT PLANT TESTS
(Runs 316, 317, and 318)

FEED COMPOSITION

Run 316 Metal-dissolver uranyl nitrate + $Th(NO_3)_4$
Run 317 10 to 1 gross weight blend of South African Concentrate and Pronto concentrate, Lot P-6.
Run 318 Pronto concentrate, Lot P-6.

STREAM CONCENTRATIONS

Aqueous Feed (AF)

Run 316 212 g/l U, 3.1N HNO_3, 3.3 g/l Th
Run 317 204 g/l U, 3.1N HNO_3, 0.32 g/l Th
Run 318 195 g/l U, 3.0N HNO_3, 3.75 g/l Th

Organic Extract (AX) 33.5% TBP-kerosene.

Scrub Stream (BS) Deionized water, room temperature

Strip Stream (CS) Deionized water, 150°F

FLOW RATES (gph)

	Run 316	Run 317	Run 318
AF	61	56	64
AX	~119	111	111
BS	14.4	16	17
CS	135	136	136

AP DENSITY

Run 316 0.998
Run 317 1.007
Run 318 1.015

PULSE CONDITIONS

Extraction (A) Column

Frequency 65 cpm
Amplitude ¾ inch

Scrub (B) Column

Frequency 50 cpm
Amplitude ⅝ inch

Final stream analyses for this test are given in Table VII. Only selected samples were analyzed for thorium because of the long analytical procedure involved. A calibration of the organic (AX) pump was not available, thus precluding material balance calculations. The stream analyses for the last part of the test are fairly constant, however, and indicate that a thorium decontamination factor of approximately 6 can be expected from the standard 33.5 per cent TBP flowsheet (AP density of 1.000). On the basis of these results, an interim specification of <350 ppm thorium on a uranium basis was established for the Refinery extraction feed stream to insure that the thorium specification was consistently met until a method for processing thorium-bearing feeds was developed.

3.2.5.2 Blending Required to Obtain Specification Product from Pronto Concentrate (Run 317) – The results of Run 316 indicated that a high blend ratio of other feed materials with Pronto concentrate is required to meet the 50 ppm thorium specification. It was the objective of the second test to determine the thorium content of the aqueous product (CP) resulting from the extraction of a 10 to 1 gross blend of South African concentrate (~60 per cent U) and Lot P-6 Pronto concentrate (53 per cent U). This blend corresponds to a 12 to 1 blend on a uranium basis. The specified run conditions for this test (Run 317) are given in Table VI.

The desired run conditions were not realized because of a failure of automatic AP density controls. The AP density could not be controlled at the desired level of 1.000, and it rose to 1.007 during the test. The results of the test (Table VII) are thus not indicative of those to be expected from normal operations. Stream analyses indicated that the thorium distribution in the system had approached equilibrium at the end of the 10-hour test. A decontamination factor of 60 was obtained to give 25 ppm thorium in the CP stream. Operation at a lower AP density level would have resulted in a higher level of thorium contamination, but the data indicated that the blend ratio used is

[redacted]

TABLE VII

FINAL STREAM ANALYSES OF PRELIMINARY PILOT PLANT EXTRACTION TESTS WITH THORIUM-CONTAINING FEEDS

Feed Composition	Run Number		
	316	317	318
	Metal Dissolver UNH + $Th(NO_3)_4$	10/1 Gross Wt Blend of S. African/Pronto (P-6)	Pronto (P-6)
Aqueous Feed (AF)			
U (g/l)	200	200	195
Th (g/l)	3.73	0.30	3.75
Th (ppm) (U basis)	18,650	1,500	19,231
AP Density	0.998	1.010	1.015
Organic Product (AP)			
U (g/l)	104	126	127
Th (g/l)	4.43	0.006	0.019
Aqueous Raffinate (AR)			
U (g/l)	0.01	0.006	3.7
Th (g/l)	—	0.370	—
Aqueous Product (CP)			
U (g/l)	84	80	85
Th (g/l)	0.26	0.002	0.0044
Th (ppm) (U basis)	3095	25	52
Thorium Decontamination Factor	6.0	60	370
Length of Test (hr)	11	10	7

approximately the one required to obtain in-specification product (<50 ppm Th) in the present Refinery system. Blending at this ratio could not be considered a feasible method of processing these concentrates, since they are expected to be available in large quantities.

3.2.5.3 Decontamination Effected by Maximum Uranium Saturation of the Organic Extract (Run 318) – Thorium-uranium separation is facilitated by high uranium saturation of the organic extract; however, high saturation in the National Lead Company of Ohio flowsheet is accompanied by high raffinate losses of uranium. As a basis for development work on the thorium-uranium separation problem, it was desirable to determine the thorium decontamination and the uranium raffinate losses resulting from the extraction of Pronto concentrate at the highest possible saturation level.

According to the distribution curve for uranium from Lot P-6 Pronto concentrate between 33.5 percent TBP and 3.0N HNO_3, the theoretical organic uranium saturation limit for the system is 125 g/l uranium (Fig. 1).

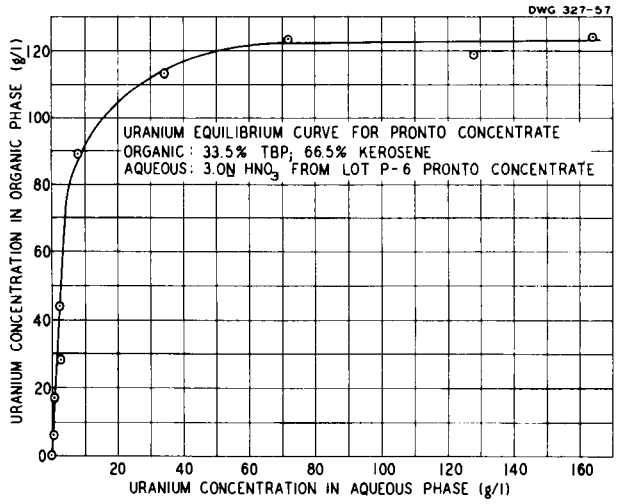

FIGURE 1 Uranium Equilibrium Curve for Pronto Concentrate

[redacted]

The nominal operating conditions for this test (Run 318) are given in Table VI. Lot P-6 Pronto concentrate was used as the feed. The objectives of the test were not fully realized because of emulsification difficulties which occurred during the latter part of the run when the aqueous feed (AF) rate was raised to insure maximum saturation.

Because of the varying feed rate during the course of this test, equilibrium throughout the extraction column was not attained in the seven hours running time. The final analyses (Table VII) showed that a thorium decontamination of at least 370, corresponding to 52 ppm thorium in the CP stream, can be obtained at a high (>99 per cent) saturation level.

The emulsification difficulties precluded a determination of the raffinate losses which would result if the feed rates were controlled so that the requirements for maximum saturation were fulfilled but not exceeded. The results indicated that with refined control, the raffinate losses might not greatly exceed 0.5 g/l uranium. Density would have to be controlled at some intermediate point in the column, rather than on the AP stream.

3.3 ROASTING STUDIES – Thorium oxide is a highly refractory material, and experience has shown that thorium oxides are, in general, more difficulty solubilized in nitric acid than are uranium oxides. Roasting experiments were therefore designed to determine whether a significant portion of the thorium content of the concentrates could be rendered acid-insoluble by roasting, without detrimental effects on uranium recovery.

A series of laboratory tests was made to determine whether the acid-soluble thorium content of concentrates such as Pronto can be reduced by roasting the concentrate prior to digestion. Samples of Pronto concentrate were roasted for one hour at 1500°F and 1800°F. The 1500°F temperature represents the limits of large-scale roasting facilities immediately available on the site.

Digestions, calculated to yield 200 g/l uranium in the digest slurry, were then made. The thorium content was determined immediately after digestion and 24 hours later.

The results, which are summarized in Table VIII, showed that roasting at 1500°F has little effect on the acid solubility of the thorium, as determined by the standard low temperature digestion technique. Roasting the ore at 1800°F results in a marked decline in the amount of acid-soluble thorium, but also causes a portion of the uranium to become insoluble. Digestion under more rigorous conditions (higher temperature) results in a slightly higher acid solubility of both thorium and uranium. Results also showed that a post-digestion reaction takes place in all the slurries, causing the thorium and uranium concentrations to approach those of the unroasted ones. Roasting for periods longer than one hour was not considered, since past experience has shown that the unconverted uranium value increases significantly when concentrates are heated for periods greater than one hour at 1500°F.

TABLE VIII

THORIUM AND URANIUM CONCENTRATIONS IN PRONTO CONCENTRATE DIGEST SLURRIES

Sample	Soluble U (g/l)	Soluble Th (g/l)
1. Unroasted	197	3.35
2. Roasted for one hour at 1500°F; standard digestion conditions*		
(a) Slurry sampled immediately	200	3.01
(b) Slurry sampled after 24 hours.	204	3.22
3. Roasted for one hour at 1800°F; standard digestion conditions*		
(a) Slurry sampled immediately	137	0.14
(b) Slurry sampled after 24 hours.	182	2.88
4. Roasted for one hour at 1800°F, digested 2 hours at 140°F		
(a) Slurry sampled immediately	155	1.06
(b) Slurry sampled after 3 days	198	3.11

*The standard digestion procedure involves no external application of heat. The rate of ore addition is controlled so that the temperature of the slurry does not exceed 140°F. After all of the ore is added, the digestion is allowed to proceed for two hours with no temperature control. The maximum slurry temperature for Samples 2 and 3 above was 120°F.

[redacted]

From these results, it was concluded that pretreatment by roasting is not a feasible method of accommodating thorium-contaminated concentrates in the TBP extraction system. Decontamination must, therefore, be achieved by process modification.

3.4 PROCESS MODIFICATIONS CONSIDERED – In addition to increased uranium saturation of the primary extract (AP) stream, which had been demonstrated as being unattractive from a uranium recovery point of view, other process modifications were possible.

Use of a uranyl nitrate (UNH) scrub stream can effect a higher decontamination of impurities in the scrub column by increasing the uranium saturation of the organic extract. The ultimate production capacity would be limited, however, by the UNH recycle.

The extraction of thorium by TBP, like that of uranium, is influenced by the acidity of the aqueous phase. In general, the distribution coefficient (O/A) of thorium increases as the acidity of the aqueous phase increases, and the effects are much more pronounced at low thorium concentrations.[12] In systems containing both thorium and uranium, the distribution coefficients of the two components vary to different degrees as the acidity changes.[13] Thus, thorium-uranium separation may be facilitated by adjusting the acidity of various extraction process streams. Reducing the acidity of the aqueous feed (AF) stream to approximately 1N would probably effect a partial separation; acidities lower than 1N would likely be detrimental to uranium extraction. The difference between the distribution coefficients of thorium and uranium may also be used to advantage in "selective stripping" operations in which thorium, which has the lower distribution coefficient (O/A), may be stripped from the organic extract by a dilute nitric acid solution and the uranium may subsequently be re-extracted by water.[14,15] Use of a selective stripping technique either in the re-extraction process or in the scrubbing operation would entail flow modifications which would probably reduce the production capacity of the extraction area and/or result in increased product acidity, with consequent corrosion problems.

At low thorium concentrations, sulfates and phosphates strongly depress thorium distribution coefficients.[16] Other agents, such as fluoride and oxalate, which form a thorium precipitate, may also be expected to reduce thorium extraction. Addition of thorium "complexing agents" to the aqueous (AF) feed stream can thus be considered as a possible method of separating thorium and uranium. Most of the agents also influence uranium extraction; hence, their use depends upon whether thorium is preferentially affected.

The use of complexing agents was considered to be the most promising approach of those considered, since it would involve only feed slurry adjustment and would neither impose capacity limitations nor necessitate extraction process changes.

3.5 THORIUM COMPLEXING STUDIES

3.5.1 Laboratory Tests – Four complexing agents for thorium were considered: phosphate, sulfate, fluoride, and oxalate.

Phosphate and sulfate have both been shown to retard the extraction of thorium by TBP, especially at low thorium concentrations.[16] The addition of phosphoric acid or sulfuric acid to a feed slurry containing thorium may result in the formation of orthophosphate or sulfate, or possibly various thorium complexes, since thorium shows a strong tendency to form complexes with anions.[17] High concentrations of phosphate and sulfate are known to retard the extraction of uranium. Successful use of these agents in the extraction system would therefore depend upon whether thorium is preferentially affected.

[redacted]

Fluoride and oxalate are used to precipitate thorium quantitatively. Both agents would be expected to affect uranium extraction, since uranyl fluoride can form in solutions containing free fluoride, and uranium can be precipitated from solution as the oxalate.

To determine the relative effects of the four reagents upon the extraction of both thorium and uranium, a series of batch equilibration tests was made upon feed slurries from Pronto Lot P-6 containing approximately 200 g/l uranium and 3.0N HNO_3. Phosphate was added as H_3PO_4 to give a total concentration of 7 percent PO_4^{-3} on a uranium basis; this concentration has been considered to be the maximum level of phosphate which can be tolerated in the extraction of relatively pure uranyl nitrate solutions by TBP without excessive raffinate losses of uranium. In another test, sufficient hydrofluoric acid was used to give 110 per cent of the stoichiometric fluoride requirements for ThF_4. The stoichiometric amount of oxalic acid required for precipitation of the thorium as $Th(C_2O_4)_2$ was added to a third slurry. Two levels of sulfate concentration were investigated: 5:1 and 10:1 molar ratios of SO_4:Th. Higher concentrations of sulfate were not investigated, since work done at Battelle Memorial Institute indicated very little additional repression of thorium extraction when the molar ratio was increased from 10:1 to 20:1;[18] in addition, scaling of the extraction column is prevented by minimizing the sulfate concentration in the aqueous feed stream.

Phosphate and fluoride were indicated to be the most promising complexing agents (Fig. 2). Uranium extraction was slightly affected in all cases (Fig. 3), but the effect was not as pronounced.

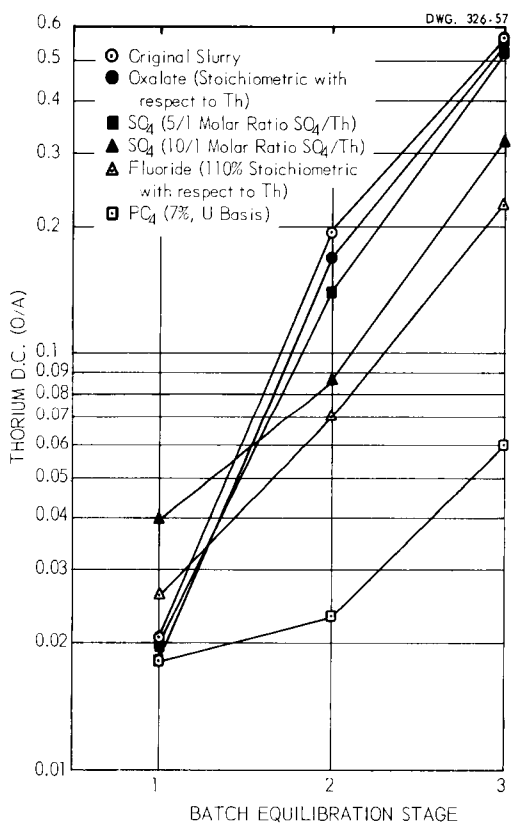

FIGURE 2 Effect of Complexing Agents Upon the Distribution Coefficient of Thorium as Determined by Batch Equilibrium Test With Pronto Feed Slurry

[redacted]

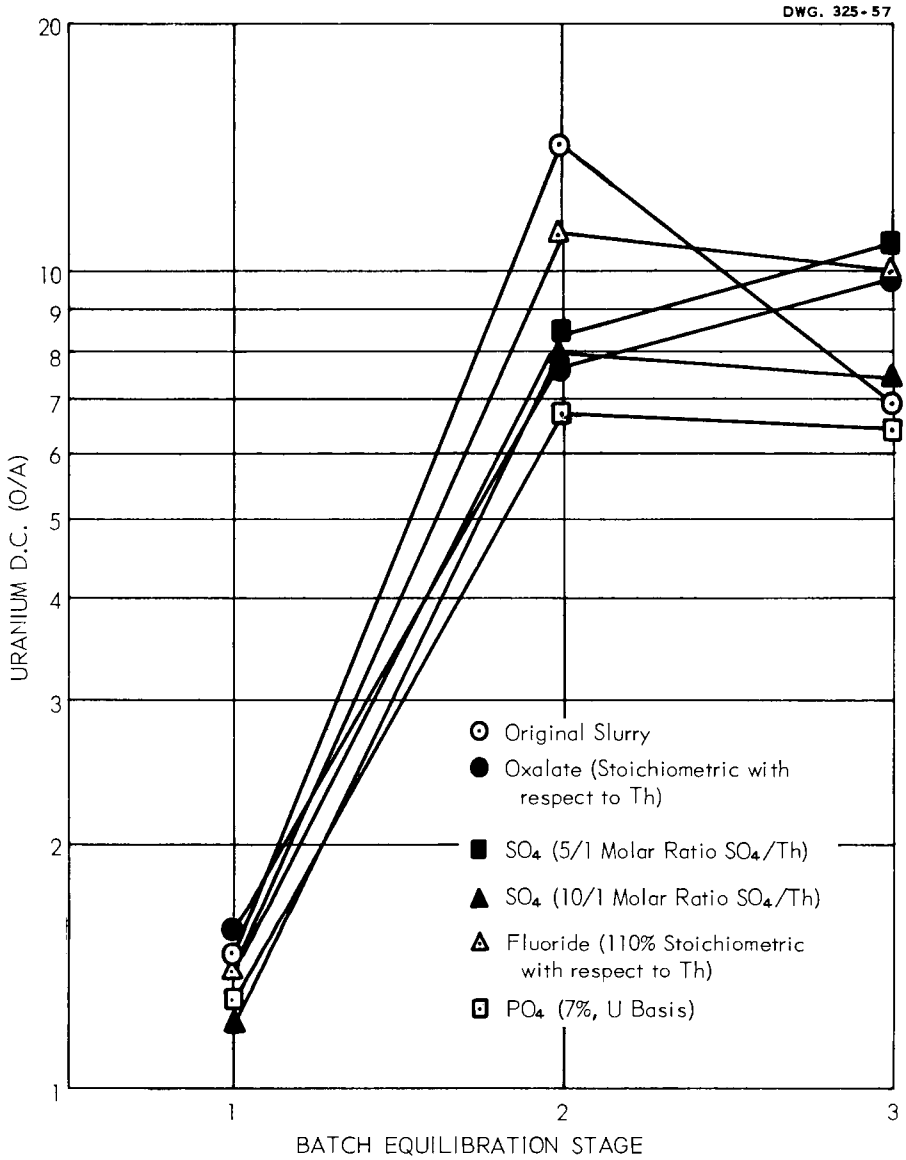

FIGURE 3 Effect of Complexing Agents Upon the Distribution Coefficient of Uranium, as Determined by Batch Equilibrium Test With Pronto Feed Slurry

3.5.2 Pilot Plant Tests

3.5.2.1 Summary of Results – On the basis of the laboratory results, pilot plant tests were conducted to determine the effectiveness of phosphate and fluoride addition to the feed slurry on the repression of thorium extraction. Phosphate, added as phosphoric acid, was shown to be more effective, and a series of tests ensued to develop the most effective means of utilizing this complexing agent.

[redacted]

The nominal operating conditions, which were held constant for all the tests, are given in Table IX. Final stream analyses are presented in Table X. The degree of product purity obtained in various tests is indicated by the spectrochemical analyses summarized in Table XI.

The series of tests showed that in-specification product (<50 ppm Th) can be obtained from feed slurries containing 2.2 per cent thorium (U basis) by the addition of phosphoric acid to give a total of 15 per cent PO_4^{-3} (U basis). The raffinate losses of uranium were only slightly affected.

3.5.2.2 Extraction Feed Materials – Most of the tests were made with Pronto concentrate Lot P-16. A shipment of Lot P-26 received for experimental purposes could not be extracted under any conditions because of emulsification, and a final test (Run 328) was made with a feed slurry spiked with $Th(NO_3)_4$.

Emulsion tendencies were also noted with Lot P-16; however, it was determined that this material could be extracted without difficulty by carefully controlling start-up conditions. The cause of the emulsification appeared to be the presence of very finely divided solids in the aqueous phase. A laboratory examination of several feed slurries derived from the same lot of concentrate showed that no precipitation occurred if phosphoric acid were added. The formation of a white precipitate in the aqueous phase was observed, however, during the initial equilibrations of a batch counter-

TABLE IX

OPERATING CONDITIONS FOR PILOT PLANT TESTS
(Thorium Complexing Studies)

FEED FOR INDIVIDUAL TESTS

Run 319 Pronto, Lot P-16 + 7% total PO_4^{-3} (U basis)

Run 320 Pronto, Lot P-16 + 7% total PO_4^{-3} (U basis)

Run 321 Pronto, Lot P-16 + Fluoride (10% excess for ThF_4)

Run 324 Pronto, Lot P-16 + 10% total PO_4^{-3} (U basis)

Run 325 Pronto, Lot P-16 + 15% total PO_4^{-3} (U basis)

Run 326 Pronto, Lot P-16 + $Th(NO_3)_4$ to give a total thorium concentration of approximately 4 g/l Th + 15% total PO_4^{-3} (U basis)

Run 327 Pronto, Lot P-26 + 15% total PO_4^{-3} (U basis)

Run 328 Metal-Dissolver UNH + $Th(NO_3)_4$ to give approximately 4 g/l Th + 15% total PO_4^{-3} (U basis)

RUN CONDITIONS FOR ALL TESTS

Streams

Aqueous Feed (AF)	200 ± 10 g/l U; 3.0 ± 0.2N HNO_3
Organic Extractant (AX)	33.5% TBP, nonacidified
Scrub Water (BS)	Deionized water, room temperature
Strip Water (CS)	Deionized water, 150°F

AP Density 1.000.

Startup Flow Rates

AF	60 gph	BS	16 gph
AX	118 gph	CS	136 gph

Pulse Conditions

A Column F = 65 cpm; A = ¾ inch

B Column F = 50 cpm; A = ⅝ inch

[redacted]

current test. The precipitate disappeared after about four equilibrations. The same phenomenon was observed in the absence of additional phosphate. The precipitate, which consisted largely of magnesium, iron, and phosphate, with very little thorium, was found to form when the acidity of the aqueous phase fell below 0.25N. It was subsequently demonstrated that if, upon start-up, the slurry is allowed to progress to the bottom of the column before the organic flow is started, the emulsion which forms dissipates after a short time, presumably as the acid profile of the aqueous phase shifts toward the bottom of the column. This start-up technique was successfully used in all subsequent extraction tests.

3.5.2.3 Phosphate Complexing Test 1 (Run 320) (U percent PO_4^{-3}, U basis) – The objective of this test was to determine the effect of a total concentration of 7 per cent phosphate upon the extraction of thorium and uranium from a Lot P-16 Pronto feed slurry.

TABLE X

SUMMARY OF PILOT PLANT EXTRACTION TESTS EMPLOYING THORIUM COMPLEXING AGENTS

Feed Composition	Run Number					
	320**	321*	324	325	326	328
	Pronto (P-16) + 7% PO_4	Pronto (P-16) + NaF	Pronto (P-16) + 10% PO_4	Pronto (P-16) + 15% PO_4	Pronto (P-16) + $Th(NO_3)_4$ + 15% PO_4	Metal – Dissolver UNH + $Th(NO_3)_4$ + 15% PO_4
Aqueous Feed (AF)						
U (g/l)	190	195	194	200	203	202
Th (g/l)	2.7	2.5	2.5	2.6	4.4	4.12
Th (ppm) (U basis)	14,210	12,820	12,886	13,000	21,622	20,430
AP Density	1.002	0.996	1.001	1.000	0.998	0.998
Organic Product (AP)						
U (g/l)	105	103	107	103	105	108
Th (g/l)	1.10	2.61	0.351	0.144	0.156	0.020
Aqueous Raffinate (AR)						
U (g/l)	0.015	0.012	0.084	0.12	0.26	0.015
Th (g/l)	1.03	1.20	1.82	2.43	3.77	3.34
Aqueous Product (CP)						
U (g/l)	86	78	84	89	78	81
Th (g/l)	0.0086	0.0260	0.0064	0.0034	0.00235	0.00273
Th (ppm) (U basis)	100	333	76	39	30	33
Thorium Decontamination Factor	142	39	171	333	720	619
Length of Test (hr)	11	12¾	12	11	12	21

*NaF added to give 110% stoichiometric F requirements for precipitation of all thorium as ThF_4.
**All phosphate concentrations are on a uranium basis.

[redacted]

No difficulties were encountered during the 11-hour test. Stream analyses (Table X) indicated that a decontamination factor of 142 was achieved, to give 100 ppm thorium in the CP stream. Raffi-(AR) losses of uranium were low, generally less than 0.02 g/l uranium. Material balance calculations indicated that uranium, but not thorium, concentrations had approached steady-state values. Spectrochemical analysis of the CP stream (Table XI) showed satisfactory product purity, within the limits of the method for the various elements. The slightly high boron and sodium values were not considered significant, since the samples were taken in glass bottles.

3.5.2.4 Fluoride Complexing Test (Run 321) – To test the effectiveness of fluoride as a complexing agent for thorium, a test was performed with sufficient NaF added to the feed slurry to give 110 per cent of the stoichiometric fluoride requirements for ThF_4.

The test proceeded without difficulties for 12¾ hours. A thorium decontamination factor of 39 was achieved, giving a CP stream containing 333 ppm thorium (Table X). Material balance calculations indicated that equilibrium had been attained for both thorium and uranium.

3.5.2.5 Phosphate Complexing Test 2 (Run 324) (10 percent PO_4^{-3}, U basis) – Since phosphate proved to be more effective than fluoride in retarding the extraction of thorium and since excessive raffinate losses were not experienced with seven per cent phosphate, the next test was designed to investigate the effect of a 10 percent total phosphate concentration. No difficulties were experienced in the 12-hour test. Use of the higher phosphate concentration raised the thorium decontamination factor to 171, giving a CP stream containing 75 ppm thorium (Table X). The AP saturation was slightly higher than desired during most of the test, but the stream analyses indicated that the raffinate losses of uranium at the desired AP density level of 1.000 would be less than 0.1 g/l uranium. Both thorium and uranium approached steady-state distribution. Spectrochemical analysis of the CP stream indicated satisfactory product purity (Table XI).

3.5.2.6 Phosphate Complexing Test 3 (Run 325) (15 per cent PO_4^{-3}, U basis) – Since no deleterious effects from high phosphate concentrations had yet been noted, a total phosphate concentration of 15 per cent PO_4 (U basis) was used in the next test.

TABLE XI

SPECTROCHEMICAL ANALYSIS* OF URANYL NITRATE (CP) PRODUCED IN PILOT PLANT TESTS

Element	Run 320	Run 324	Run 325	Element	Run 320	Run 324	Run 325
Al	<4	<4	<4	Mo	<4	<4	<4
B	0.2	0.25	<0.2	Na	25	15	15
Bi	<1	<1	<1	Ni	<2	<2	4
Cd	<0.2	<0.2	<0.2	P	<20	<20	<20
Co	<2	<2	<2	Pb	<1	<1	<1
Cr	<1	<4	<4	SiO_2	<20	<20	<20
Cu	<1	<1	<1	Sn	<1	<1	<1
Fe	12	6	10	V	<20	<20	<20
Mg	4	4	3	Zn	<20	<20	<20
Mn	<4	<4	<4				

*All values are ppm, uranium basis.

[redacted]

A decontamination factor of 333 was achieved to give an in-specification product (39 ppm, U basis) (Table X). Raffinate losses of uranium averaged 0.15 g/l U. Again, material balance calculations indicated that equilibrium with respect to thorium and uranium distribution had been attained. Satisfactory product purity was demonstrated (Table XI).

3.5.2.7 Phosphate Complexing Test 4 (Run 326) (15 per cent PO_4^{-3}, U basis) – Specification product was obtained in Run 325 through the use of 15 per cent phosphate; however, the thorium content of the feed slurries from Lot P-16 Pronto was less than the maximum 2.3 per cent thorium (U basis) expected. Therefore, the test conditions were next imposed upon a Pronto feed slurry spiked with $Th(NO_3)_4$; the AF stream for this test contained 2.16 per cent thorium (U basis).

A satisfactory product was again obtained (Table X). The CP stream contained 30 ppm thorium (U basis), which represented a thorium decontamination factor of 720. Raffinate losses of uranium were slightly higher than those obtained in Run 325 (0.25 g/l U). Both thorium and uranium approached steady-state distribution.

3.5.2.8 Thorium Equilibrium Test (Run 328) (15 per cent PO_4^{-3}, U basis) – The preceding tests each lasted approximately 12 hours. In most cases, material balance calculations based on stream concentrations and calculated flows indicated that equilibrium with respect to thorium distribution in the system had been reached during this time. This factor is demonstrated particularly well by the results of Run 326, which are given in detail in Table XII. The results obtained in the 12-hour tests were considered sound, although it is known that thorium equilibrium is slowly attained. It was thus possible that a slow build-up of thorium in the parts per million range could occur without being detected in the material balance calculations. A 21-hour extraction test (Run 328) was therefore made to determine whether the favorable results previously obtained could be duplicated in an extended testing period. Metal-dissolver product was used as the uranium feed stream, and $Th(NO_3)_4$ was added to give approximately 4 g/l thorium. Phosphoric acid was added to the feed hold tank so that the phosphate concentration in the feed was 15 per cent PO_4^{-3} (on a uranium basis).

Although relatively pure feed was used, no deleterious effects due to the high phosphate concentration were noted. Raffinate losses (0.015 g/l U) were lower than had been experienced in Runs 325 and 326, in which the same nominal phosphate concentration was used. The thorium content of the CP stream was again within specification (33 ppm Th, U basis) and the thorium decontamination factor was 619 (Table X). Material balance calculations indicated that both thorium and uranium had approached equilibrium distribution at the end of the 21-hour test.

On the basis of these results, it was concluded that when the phosphate complexing technique is used, valid thorium results can be obtained in 12-hour extraction tests.

3.6 PLANT DEMONSTRATION OF THE PHOSPHATE-COMPLEXING TECHNIQUE – Upon the completion of the development tests described above, the phosphate complexing technique was demonstrated in the National Lead Company of Ohio Refinery with feed blends comprised in part of thorium-containing concentrates, such as Pronto, Bicroft, Faraday, Denison and Porter Brothers. Although in most cases, the thorium content of the extraction feed stream was less than the amount which was used as the basis for the development program (2 per cent Th, U_3O_8 basis), the decontamination achieved in all cases indicated that specification product can be obtained from feed slurries containing this amount of thorium and 15 per cent phosphate, on a uranium basis. For example, in one test with Porter Brothers concentrate, an aqueous product with 111 ppm thorium was

[redacted]

TABLE XII

SUMMARY SHEET FOR PILOT PLANT RUN 326
Pronto Lot P-16 + $Th(NO_3)_4$ + H_3PO_4(15% PO_4, U Basis)

Clock Time	Hour of Run	Aqueous Feed (AF)			AP Density	Organic Product (AP)			Organic Profile Samples					Aqueous Raffinate (AR)			Scrub Recycle (BR)		Scrubbed Organic Product (BP)	Aqueous Product (CP)			Material Balances for Extraction Column (% Closure)	
		U (g/l)	Th (g/l)	HNO_3 (N)		U (g/l)	Th (g/l)	HNO_3 (N)	A-5 (g/l U)	A-4 (g/l U)	A-3 (g/l U)	A-2 (g/l U)	A-1 (g/l U)	U (g/l)	Th (g/l)	HNO_3 (N)	U (g/l)	Th (g/l)	U (g/l)	U (g/l)	Th (g/l)	Th (ppm)	U	Th
1300	1	204	4.19	2.8	1.003	112		0.23						0.85		2.5	64.9		67	46.7				
1400	2	210		3.0																				
1500	3				1.017	118		0.23						0.68		2.5	125							
1600	4	205		3.1	1.012	117		0.19	108.2	58.3	13.0	4.4	0.80	0.68		2.4	141		76	72.5				
1700	5				1.013	122		0.30						0.68		2.5	144							
1800	6	204	4.30	3.1	1.013	121		0.16						0.23		2.6	161		82	73.7				
1900	7				1.014	122	0.0478	0.30						0.82	3.76	2.5	175	0.425		78.2	0.00113	14.5	100.2	107.6
2000	8	203		3.1	1.011	119		0.31	104.5	33.2	8.0	2.9	1.2	0.20		2.2	187		90					
2100	9		4.44		0.999	111		0.37						0.19		2.2	180							
2200	10	204		3.2	0.994	106	0.190	0.37						0.14	3.65	2.3	106	1.03	87	87.9	0.00229	26.1	95.1	102.1
2300	11				0.997	112	0.156	0.36						0.22	3.75	2.5	87.0	1.23		77.3	0.00209	27.0	102.9	101.9
2400	12	203	4.40	3.2	0.998	112	0.156	0.26	92.3	31.5	5.5	1.8	0.22	0.26	3.77	2.6	91.1	1.23	84	77.8	0.00235	30.2	102.3	102.4

NOTES

1. *Actual Flow Rates*

   AF Flow: 1840 (Measured at 55 gph)
   AX Flow: 2015 (Measured at 110 gph)
   2230 (Measured at 111 gph)

2. *Thorium Decontamination*

   Original Th Conc. 4.4 g/203.5 g U 21,622 ppm.
   CP Th Conc. 30 ppm
   Decontamination Factor 720

obtained from a feed slurry containing 4.5 per cent thorium and 11.3 per cent phosphate (all on a uranium basis).[19]

Thorium analyses upon plant samples were made according to a number of analytical procedures developed by the National Lead Company of Ohio Analytical Department for the routine determination of thorium in uranium process streams. A description and evaluation of these procedures will be published in a separate report.[20]

3.6.1 Extraction of Pronto Concentrate – No emulsification difficulties were encountered with Pronto concentrate received for plant processing, in contrast to experience with some of the material received for development purposes.

Application of the phosphate method of complexing thorium in uranium feed slurries is demonstrated by data presented in Table XIII, which summarizes the results obtained during the routing processing of a feed slurry composed of Pronto concentrate, Colorado concentrates, and black oxide. The stream analyses presented in the table are the averages of three consecutive hourly values, which were all essentially constant (indicating steady-state distribution of the various components in the system). Material balance calculations also indicated that the system was at steady-state during the sampling period. With 12.9 per cent PO_4^{-3} in the feed slurry, a thorium decontamination factor of approximately 200 was achieved to give 40 ppm thorium in the aqueous uranyl nitrate stream.

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TABLE XIII

PLANT DEMONSTRATION OF PHOSPHATE METHOD OF COMPLEXING THORIUM

FEED MATERIALS Pronto Concentrate (Lots 51, 52, and 55) (~ 73% (U basis); Colorado Concentrate) (~ 21% (U basis); and Black Oxide ~6% (U basis)

PHOSPHATE SOURCE H_3PO_4

Stream	U (g/l)	Th (g/l)	ppm Th (U basis)	HNO_3 (N)	PO_4^{-3} (g/l)	% PO_4^{-3} (U basis)	TBP (%)
Organic Extractant (AX)	0.68	0.0003	7900	< 0.01			32.1
Aqueous Feed (AF)	181	1.43		2.8	23.3	12.9	
Aqueous Raffinate (AR)	0.07	1.03		1.9			
Organic Extract (AP)	97	0.185		0.33			
Scrubbed Organic Extract (BP)	85	0.0045		0.04			
Aqueous Scrub Recycle (BR)	71	1.17		1.7			
Aqueous Product (CP)	86	0.0034	40	0.04			
Organic Raffinate (CR)	0.68	0.0002		< 0.01			

3.6.2 Treatment of High-Phosphate Raffinate – The aqueous raffinate from the extraction column is processed to recover nitrate values as nitric acid according to the previously published procedure.[2] Laboratory tests and actual plant experience have indicated that the presence of phosphate in raffinates in the amounts required by this method does not interfere with nitric acid recovery.

3.6.3 Direct Materials Cost for Phosphate Complexing – The phosphate concentrations reported are total values. That is, sufficient H_3PO_4 was added to the feed slurry so that the added phosphate plus the phosphate present in the feed material totaled 7 per cent, 10 per cent, or 15 per cent on a uranium basis. The amount of complexing agent required to provide the 15 per cent PO_4^{-3} concentration with different feed materials will thus vary, according to the phosphate concentration of the different concentrates. There is a possibility that >15 per cent PO_4^{-3} will be required for feed materials containing large amounts of other constituents, such as iron, which also form complexes with phosphate. The 15 per cent values appears adequate for the thorium-containing concentrates currently in production, however.

The current cost of phosphoric acid requirements for various feed materials is shown in Table XIV. A cost of about one cent per pound of uranium is indicated for feed materials containing low amounts of phosphate. It was determined in plant practice that high-phosphate feed materials, such as the uranyl ammonium phosphate (UAP) product from the National Lead Company of Ohio Scrap Recovery Plant,[21] can be utilized to provide the phosphate requirements. The cost of the complexing may therefore be considerably less than one cent per pound, depending upon the phosphate content of the concentrate and the availability of high-phosphate feed materials.

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TABLE XIV

H_3PO_4 COST FOR COMPLEXING THORIUM IN VARIOUS FEED MATERIALS

Analysis (U basis)	Pronto, P-16 (45% U)	Algom (66% U)	Bicroft (54% U)	Feed Material with no PO_4
Thorium (%)	1.73	0.55	0.85	2.00
PO_4 (%)	4.27	1.10	0.55	none
On Basis of 100 lb U				
PO_4 required (lb)	15.0	15.0	15.0	15.0
PO_4 in Concentrate (lb)	4.3	1.1	0.55	—
PO_4 to be added (lb)	10.7	13.9	14.45	15.00
H_3PO_4 to be added (lb)	11.0	14.33	14.9	15.46
75% H_3PO_4 to be added (lb)	14.6	19.1	19.85	20.56
75% H_3PO_4 to be added (gal)	1.11	1.45	1.50	1.56
Cost of 75% H_3PO_4 added*	$0.74	$0.97	$1.01	$1.04

*Cost of 75% H_3PO_4 (technical grade) delivered in 300-gal tank truck = $101.65/ton
= $ 0.0508/lb.

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4.0 CONCLUSIONS

The program described in this report was directed toward the development of methods to produce specification uranium product (<50 ppm Th, U basis) from concentrates containing 2 per cent thorium (U_3O_8 basis) in the National Lead Company of Ohio tributyl phosphate extraction system. On the basis of the results detailed in Section 3.0, the following conclusions can be made concerning the processing of such concentrates in this system.

1. Specification uranyl nitrate can be obtained without excessive losses of uranium by tributyl phosphate extraction of feed slurries containing a total phosphate content of 15 per cent PO_4^{-3} (U basis).

2. Although fluorides and phosphates repress the extraction of both thorium and uranium, the amounts can be controlled to affect thorium preferentially; phosphate, however, is the more effective agent.

3. The use of phosphoric acid as the complexing agent with 2 per cent thorium feeds will result in an additional direct materials cost of one cent (maximum) per pound of uranium. This cost can be reduced by utilizing high-phosphate concentrates as blending agents.

4. Extraction of thorium-containing feed according to the standard (without added phosphate) National Lead Company of Ohio 33.5 per cent TBP flowsheet (81 per cent uranium saturation of the organic extract) results in a thorium decontamination factor of approximately 6, in contrast to the factor of 470 required. With this flowsheet, thorium-bearing concentrates must therefore be blended approximately 1 to 12 with other high-grade concentrates in order to meet the 50 ppm thorium specification.

5. The thorium decontamination factor can be increased to 370 without added phosphate by operating at a high uranium saturation level (approximately 99 per cent); however, high raffinate losses of uranium occur. With proper density control, raffinate losses might be maintained at 0.2 to 0.5 g/l uranium at this saturation level.

6. Roasting of the concentrates under conditions favorable to uranium recovery does not reduce the acid-soluble (extractable) thorium content.

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